

NASA Technical Memorandum 104562

**Analysis of Yttrium-Barium-Copper-
Oxide by X-ray Diffraction
and Mechanical Characterization**

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and Mechanical Characterization**

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Section I: Introduction

The efforts of developing high-temperature superconductor (HTSC) Yttrium-Barium-Copper-Oxide ($\text{YBa}_2\text{Cu}_3\text{O}_7$) electrical leads are for the benefit of future NASA missions carrying payloads with sensitive instruments operating at cryogenic temperatures. Present-day leads made from copper or manganin are responsible for as much as 50 percent of the parasitic heat load on cryogenic systems. A reduction of this problem could be achieved with replacement of the conventional materials with HTSC ceramic electrical leads. An increase in the efficiency of the cryogenic cooling systems would also result. This is due to the fact that HTSC materials are excellent electrical conductors in the superconducting state, while their ceramic nature makes them good thermal insulators.

Superconductor quality has become a great concern in the industry, and it is important to develop methods to more easily evaluate these materials. The factors that need to be examined should include purity of the material, mechanical properties such as strength and Young's modulus, and the ability to exhibit the desired superconducting properties below the critical temperature. For example, Yttrium-Barium-Copper-Oxide displays superconducting characteristics at reduced temperatures only for a small

range of oxygen content. As the oxygen level is decreased from 7, the material undergoes a phase transformation at 6.6 from orthorhombic to tetragonal[1], and is no longer superconducting at any temperature.

Several methods were applied to examine this material in the present study. First, thermogravimetric analysis was used to obtain varying oxygen levels. X-ray diffraction determined purity of the samples. This technique was also used to detect the slight shifts observed in some of the diffraction peaks when the oxygen content was varied. From the angular positions of the diffraction peaks, the unit cell volume can be calculated[2]. A master curve was then generated of oxygen level versus unit cell volume. This provided a non-destructive method for determining this aspect of superconductor quality.

Mechanical properties were evaluated, first using a standard Instron Tensile Tester, and then non-destructively with laser-generated ultrasound. The objective for this analysis was to determine the average tensile strength and Young's modulus of the HTSC material and to compare them to those values for copper and manganin. Specimens for evaluation were obtained from Argonne National Labs, Clemson University, HiTc Superconco Inc., and Superconductive Components Inc., as well as those made in-house at NASA Goddard Space Flight Center.

Section II: Thermogravimetric Analysis

The thermogravimetric analyzer (TGA) can detect the weight change of a material as a function of temperature. This method can therefore measure the shifts in weight associated with the oxidation and reduction of Yttrium-Barium-Copper-Oxide.

A DuPont 951 Thermogravimetric Analyzer was used to condition the HTSC material to different oxygen levels. An alumina pan was used to hold the specimens. Before each test, the pan was heat conditioned at 1000°C to remove moisture and other contaminants. The samples examined here were from the same lot of HTSC material made by Superconco.

Specimens were purged with a gas composition consisting of 10% nitrogen and 90% hydrogen at a flow rate of 25 milliliters per minute to reduce the oxygen content. Heating rate was set at 3°C per minute to a different temperature plateau for each specimen tested, namely 400°C, 550°C, 700°C, and 940°C, as shown in Figure 1. When the desired temperature was reached, each sample was put on isothermal hold for 20 minutes, and then allowed to cool to room temperature. By reducing at different temperatures, it was possible to vary the oxygen content of this set of specimens to the levels shown in Figure 1. The next step was to examine each of these samples by x-ray diffraction to observe any shifts in the diffraction peaks caused by different oxygen levels.

Section III: X-ray Diffraction

X-ray analysis on the samples was performed using a Scintag x-ray diffractometer controlled by a DEC MicroVAX computer. The type of data collection used was a time averaging method[4], where multiple x-ray scans on the specimen being analyzed were collected. The intensity data at each angular position of 2θ for each scan was added together. At the end of data collection, each intensity was divided by the number of scans to arrive at the correct count rate. Background intensity corrections were then performed. The entire data collection process was controlled by the MicroVAX computer.

Purity of the various samples was established by comparing the measured x-ray diffraction data with that of a reference standard pattern published by researchers at the National Institute of Standards and Technology (NIST)[1], and the University of Alabama[3]. Figure 2 shows a typical scan of a powder sample having reasonably good purity. This is contrasted with Figure 3, which shows a sample with a multitude of extraneous peaks indicating impurities. Figures 4 through 6 show the x-ray diffraction patterns of some other representative specimens. Note that the sample shown in Figure 4 has 15 percent silver to increase ductility. The sample seen in Figure 6 shows a higher level

of contamination by small amounts of other compounds, notably copper oxide and barium oxide, as indicated by the extra peaks. However, all the samples examined showed an acceptable degree of purity in that their superconducting performance should not seriously be impeded.

A series of oxygen annealing and hydrogen reduction steps were performed to provide a set of samples with varying levels of oxygen content. Each sample was then analyzed by x-ray diffraction, and from the small but measurable shift in peak positions, the lattice parameters and hence, unit cell volumes were calculated[5]. A correlation curve was determined of unit cell volume versus oxygen level in the material. This enables an important aspect of the superconductor quality to be determined fairly readily by x-ray diffraction analysis.

The following table shows the calculated unit cell volumes for the various stages of treatment corresponding to different oxygen content x of the material $Y-Ba_2-Cu_3-O_x$.

TABLE 1. Lattice parameter data.

OXYGEN CONTENT (x)		a(A)	b(A)	c(A)	VOL(A ³)
O ₂ annealed	7.5	3.8105	3.8806	11.6695	172.56
As received	6.9	3.8192	3.8852	11.6778	173.28
H ₂ red. at 400°C	5.7	3.8524	3.8518	11.8221	175.42
H ₂ red. at 550°C	4.9	3.8562	3.8558	11.8256	175.83
H ₂ red. at 650°C	4.3	3.8569	3.8574	11.8265	175.95

The distribution of oxygen level covers a range from approximately 4.3 for the sample reduced at 650°C to 7.5 for the oxygen annealed specimen. The as-received sample has an oxygen level of 6.9, while those reduced at 400°C and 550°C correspond to levels of about 5.7 and 4.9, respectively. It can be seen in Figure 7 that the unit cell volume systematically increases, though by a very small amount, as the oxygen content in the material decreases. The superconducting range of $O_{6.6}$ to $O_7[1]$ corresponds to a unit cell volume of approximately 173.3 \AA^3 to 173.7 \AA^3 . Any sample can now be tested by using x-ray diffraction to evaluate its unit cell volume and observing if the value is within this acceptable range. As the oxygen content decreases from one level to another, the oxidation state of the copper changes, and accompanying this change is an increase in the radius of the copper ions[1]. This correlates with the observed increase in unit cell volume with oxygen depletion. Note that for all the samples that have undergone hydrogen reduction and have oxygen levels of 6 or less, the lattice parameters a and b have become nearly the same, as seen in Table 1. This indicates that the phase transformation from orthorhombic to tetragonal has occurred as expected. These specimens are not superconducting at any temperature.

The crystal lattice arrangement is not the only variable that determines superconductor quality. Oxygen

levels above 7 are also deemed to be detrimental. At an oxygen content of 7, the lattice structure of this material is fully saturated. More oxygen can cause strains in the lattice which adversely affect superconducting ability[3].

Using this correlation curve of oxygen content versus unit cell volume, the oxygen level of representative as-received wire specimens from the various sources was determined. As stated earlier, the desired superconducting range for oxygen level is $O_{6.6}$ to O_7 . Table 2 shows the unit cell volume and oxygen level for five different samples. The oxygen content for each is acceptable.

TABLE 2. Unit cell volume and oxygen level for HTSC samples.

Sample	Unit Cell Vol. (Angstroms) ³	Oxygen Level
Argonne Labs	173.1	7.0
Clemson Univ.	173.3	6.9
NASA/GSFC	173.4	6.9
Superconco	173.3	6.9
Supercon. Comp.	173.2	7.0

Although no systematic study has been undertaken as of this time regarding the long-term stability of these materials with respect to oxygen loss and/or gain under ambient conditions, it has been observed that samples that have undergone treatment have remained stable for the past 2 years while stored at room temperature.

Section IV: Mechanical Measurements

Mechanical testing of the HTSC electrical leads was done using a standard Instron tensile tester to obtain their tensile strength and Young's modulus. Samples in the form of cylindrical rods were tested using a 9072-kg (20000 lb) load cell, with increasing tension at a fixed rate. The Instron recorded applied load vs. sample deflection. All tests were conducted at room temperature. Five samples from each vendor were tested to get a reasonable distribution of measurements. Table 3 shows the average Young's modulus E and the average strength for each set of specimens. The results show some scatter, as is typical for this type of data with ceramics. Yttrium-Barium-Copper-Oxide is an excellent electrical conductor in the superconducting state, while its ceramic nature makes it a good thermal insulator. Unfortunately, it is these same ceramic properties that give the HTSC leads their brittleness and low strength. The Young's modulus of the HTSC wires is 60 to 80 percent of that reported for copper, however the amount of elongation that the material can withstand before fracture is far smaller, less than 10 percent that of copper. The tensile strength of these current leads is only 3 to 6 percent of the values reported for manganin and copper. The addition of 15 percent silver in the specimens from Argonne is

clearly of mechanical benefit. The average Young's modulus of these samples is higher than the others, and the tensile strength is almost twice as high as the next closest set of specimens (see Table 3). The silver does cost a slight penalty in terms of thermal conductivity[7], but this effect is more than compensated with the improved mechanical performance.

Table 3. Young's modulus and tensile strength.

Sample	Average E (GPa)	Average Strength (MPa)
Argonne Labs	90 +/- 10	20 +/- 10
Clemson Univ.	70 +/- 12	7 +/- 4
NASA/GSFC	77 +/- 8	10 +/- 5
Superconco	84 +/- 11	12 +/- 6
Supercon. Comp.	80 +/- 15	9 +/- 5

It was desired to obtain the Young's modulus of this material non-destructively, and to compare the results to those obtained by the Instron shown above. The method chosen was that of laser-generated ultrasound. The ultrasonic velocity was determined for the different HTSC wire samples, and from this, the Young's modulus E was calculated by the equation $E = \rho v^2$ [6], where ρ is the density and v is the ultrasonic velocity. The experimental arrangement for determining ultrasonic velocity is shown in

Fig. 8. A Q-switched Nd-YAG laser was used to produce pulses of approximately 15 nanoseconds duration and 20 millijoules energy. These pulses generated stress waves in the samples by the rapid deposition of energy caused by their impact. The coherent radiation generated by the laser had a wavelength of 532 nm. The light was focused and aimed at the specimens, which were positioned vertically and perpendicular to the direction of the beam. A piezoelectric transducer was clamped near the top of the sample to detect the acoustic wave generated upon impact of the laser pulse on the HTSC wire. A sampling oscilloscope was triggered when the laser was fired by the signal from a photodiode placed near the specimen and facing the beam. The signal from the transducer was amplified and filtered, and then recorded at a 20-nanosecond sampling period. From this was obtained a time of flight, measured as the difference in time between the trigger of the photodiode and the arrival of the acoustic wave at the transducer. The velocity of the acoustic wave was determined by dividing the difference between two distances from laser impact to transducer by the difference in corresponding times. The results of the ultrasonic measurements compared to those made by Instron are shown in Table 4. As before, these results are the averages of five specimens per vendor.

Table 4. Young's modulus (Instron vs. Ultrasonic).

Sample	Avg. E (GPa) [Instron]	Avg E (GPa) [Ultrasonic]
Argonne Labs	90 +/- 10	85 +/- 4
Clemson Univ.	70 +/- 12	62 +/- 7
NASA/GSFC	77 +/- 8	74 +/- 6
Superconco	84 +/- 11	80 +/- 5
Supercon. Comp.	80 +/- 15	78 +/- 9

The Young's moduli determined by the ultrasonic method are all slightly lower than those obtained by the Instron. In addition, the statistical scatter is significantly lower using the non-destructive approach.

Much work is now being done in the industry to improve the admittedly poor mechanical performance of ceramic HTSC wires. It is hoped that a far superior set of products will be available in the near future.

Section V: Summary

Much has been accomplished during the past 2 years of work on $\text{Y-Ba}_2\text{-Cu}_3\text{-O}_7$. Knowing that oxygen content plays a crucial role in superconducting ability for this material, a quality-control method for determining this quantity by x-ray diffraction was devised. Next, the focus of the investigations changed from general bulk samples of the material to wire samples specifically being designed as electrical leads and ground straps. A test program was set up with the goal of space-flight qualification of these current leads. This program included x-ray, mechanical, and electrical and thermal examination[7]. The results to this point have been encouraging. Samples obtained this year have had superior purity to those originally examined. All have had acceptable oxygen levels. A non-destructive method (laser-generated ultrasound) has been successfully used to determine Young's modulus, in addition to conventional mechanical testing. Although the Argonne samples have achieved an increase in strength and modulus through the addition of silver, much work still needs to be done to improve the mechanical properties of such wires before they can be qualified for space flight on future NASA missions.

Section VI: References

- 1) W. Wong, et al., X-ray Powder Characterization of $\text{YBa}_2\text{Cu}_3\text{O}_7$, Advanced Ceramic Materials, Vol. 2, 1987.
- 2) B.D. Cullity, Elements of X-ray Diffraction, Addison-Wesley, 1978.
- 3) D. Robinson, et al., Superconductivity, SEM, TGA, EPR, and X-ray Diffraction of $\text{YBa}_2\text{Cu}_3\text{O}_7$, Journal of Chemical Physics, 1987.
- 4) D. McLachlan, X-ray Crystal Structure, McGraw-Hill Book Co., 1957.
- 5) N. Ashcroft and N. Mermin, Solid-State Physics, Saunders College, 1976.
- 6) H. Jiang, P. Arsenovic, R.K. Eby, J.M. Liu, and W.W. Adams, Polymer, Japan, No. 36, 1987.
- 7) C. Powers, P. Arsenovic, and G. Oh, Electrical, Mechanical, and Thermal Characterization of High- T_c Superconducting Current Leads, Second World Congress on Superconductivity, 1990.

SAMPLE: SUPERCONDUCTOR #1
SIZE: 82.5050 mg
METHOD: SUPERCONDUCTOR
COMMENT: 3°C/MIN TO 940°C; HYDROGEN REDUCTION; 90%H2 10%N2

FILE: A: SUP1.02
OPERATOR: JEM
RUN DATE:

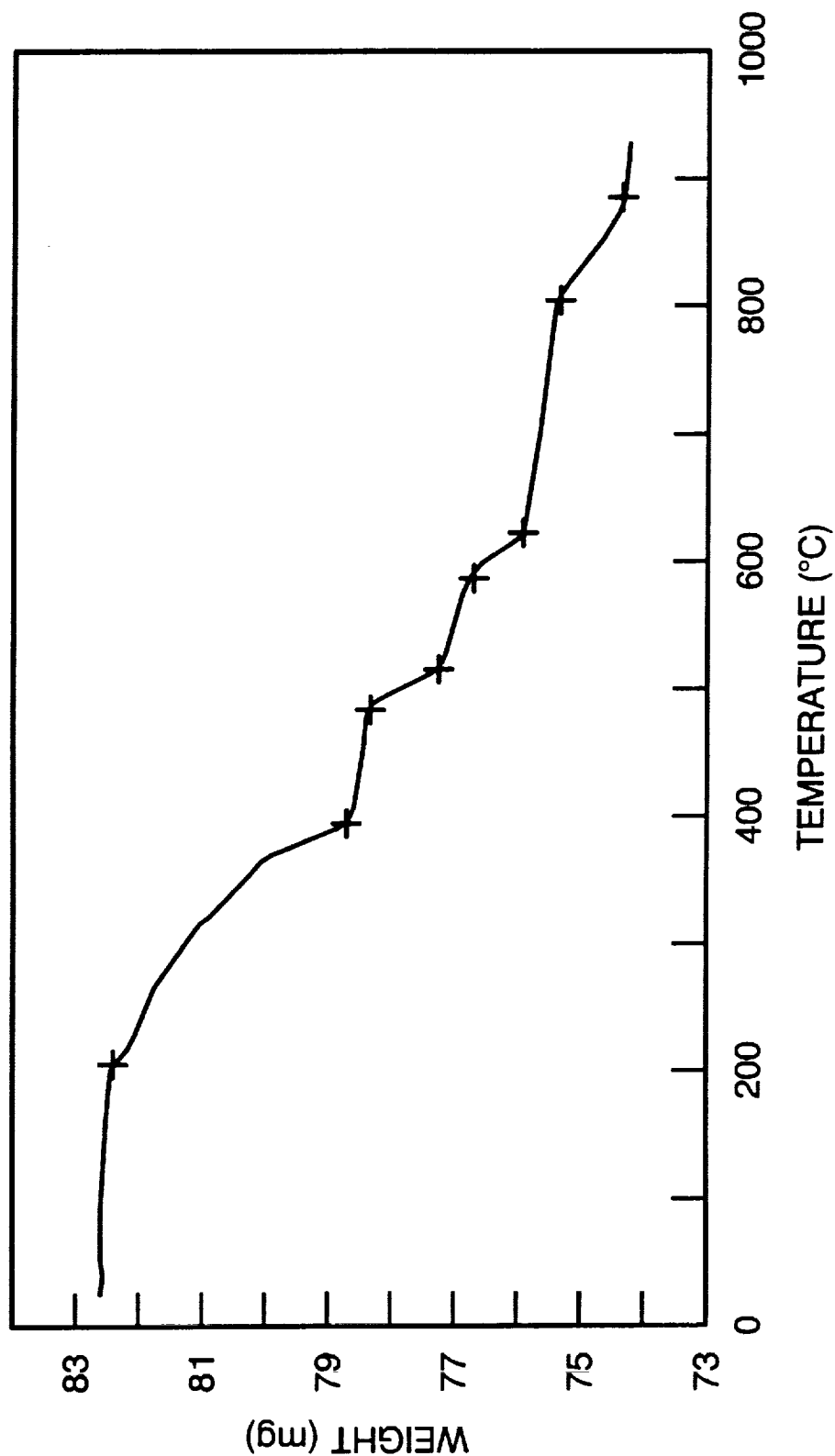


Figure 1. TGA of HTSC sample.

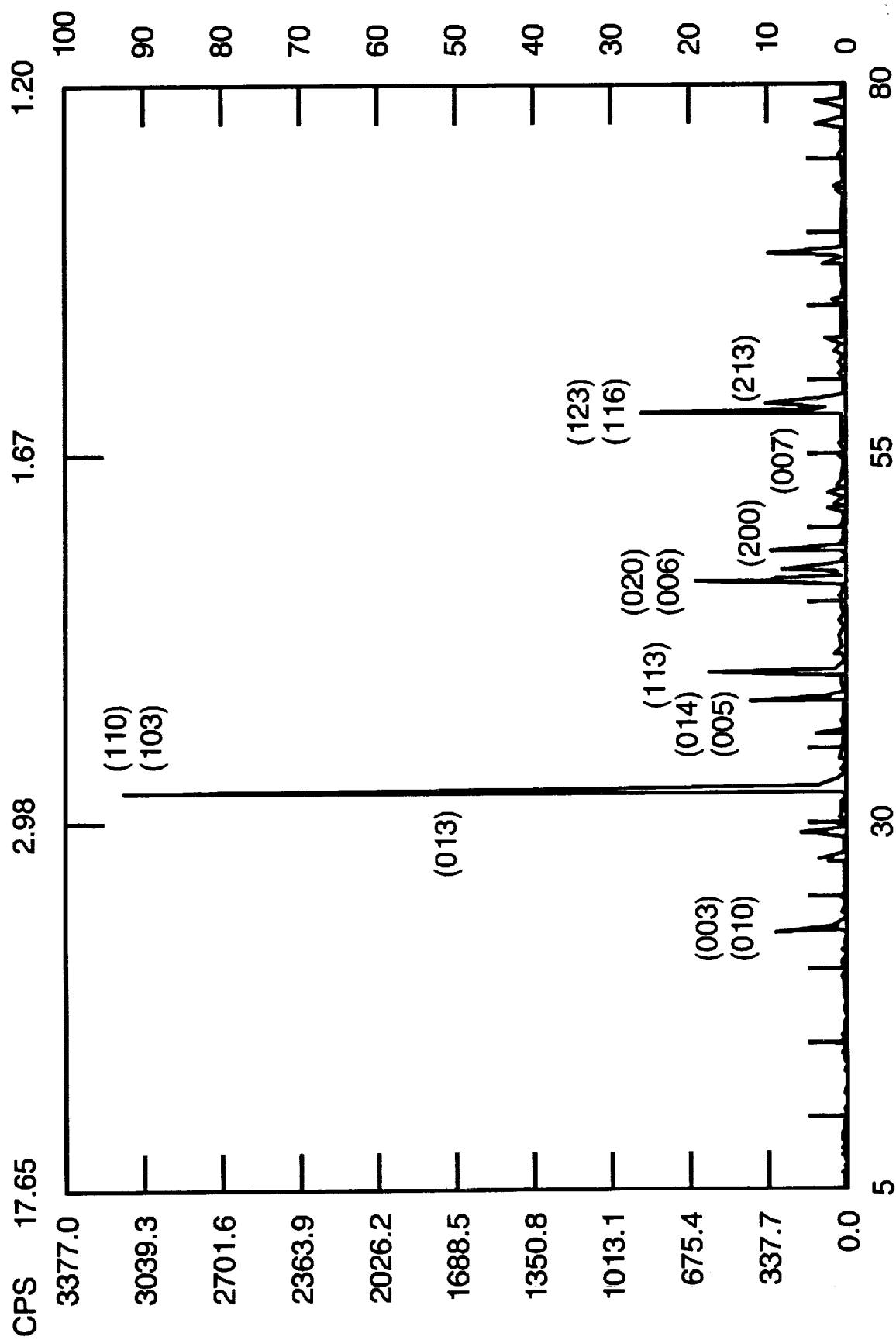


Figure 2. XRD scan of HTSC sample with good purity.

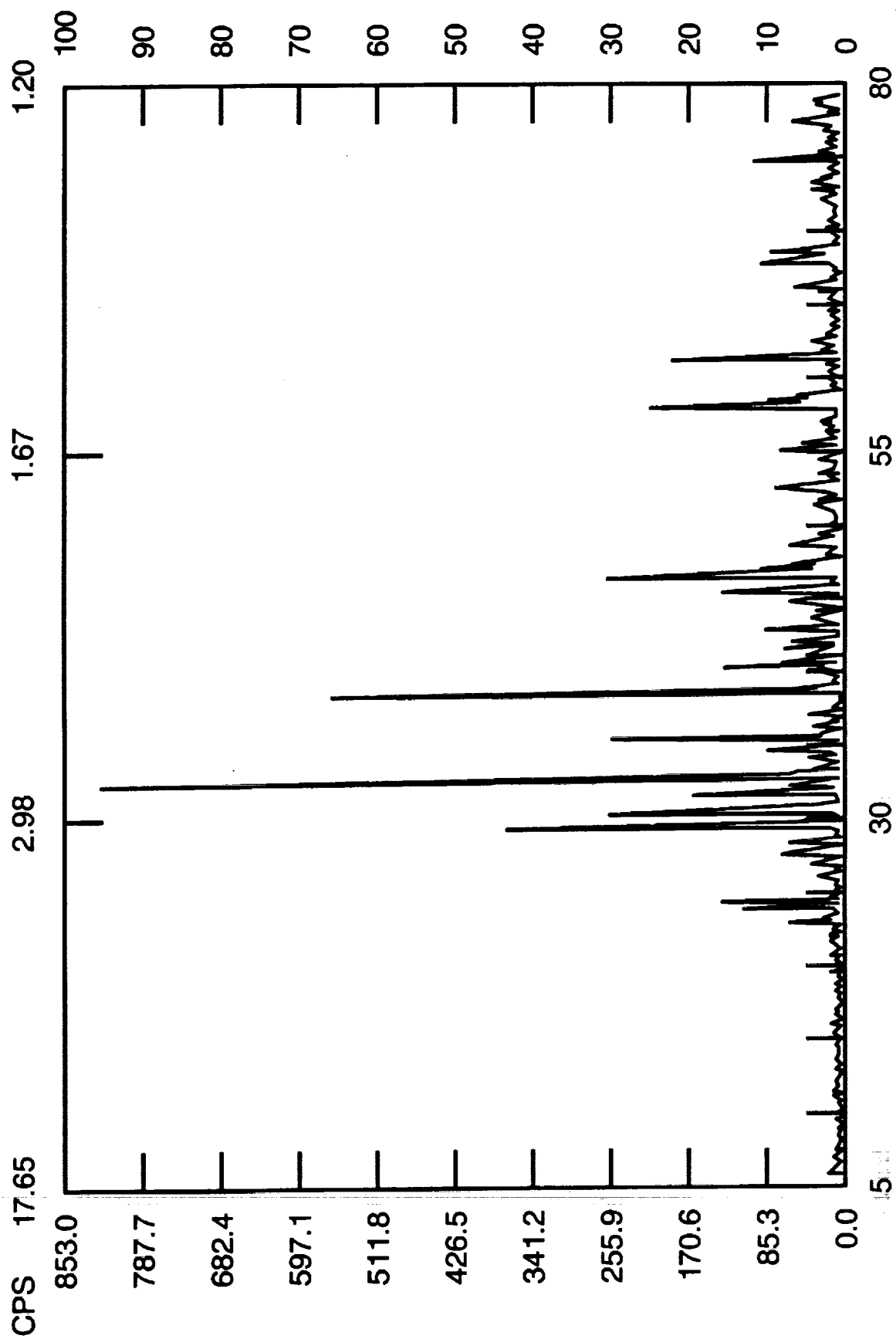


Figure 3. XRD scan of HTSC sample with many impurities.

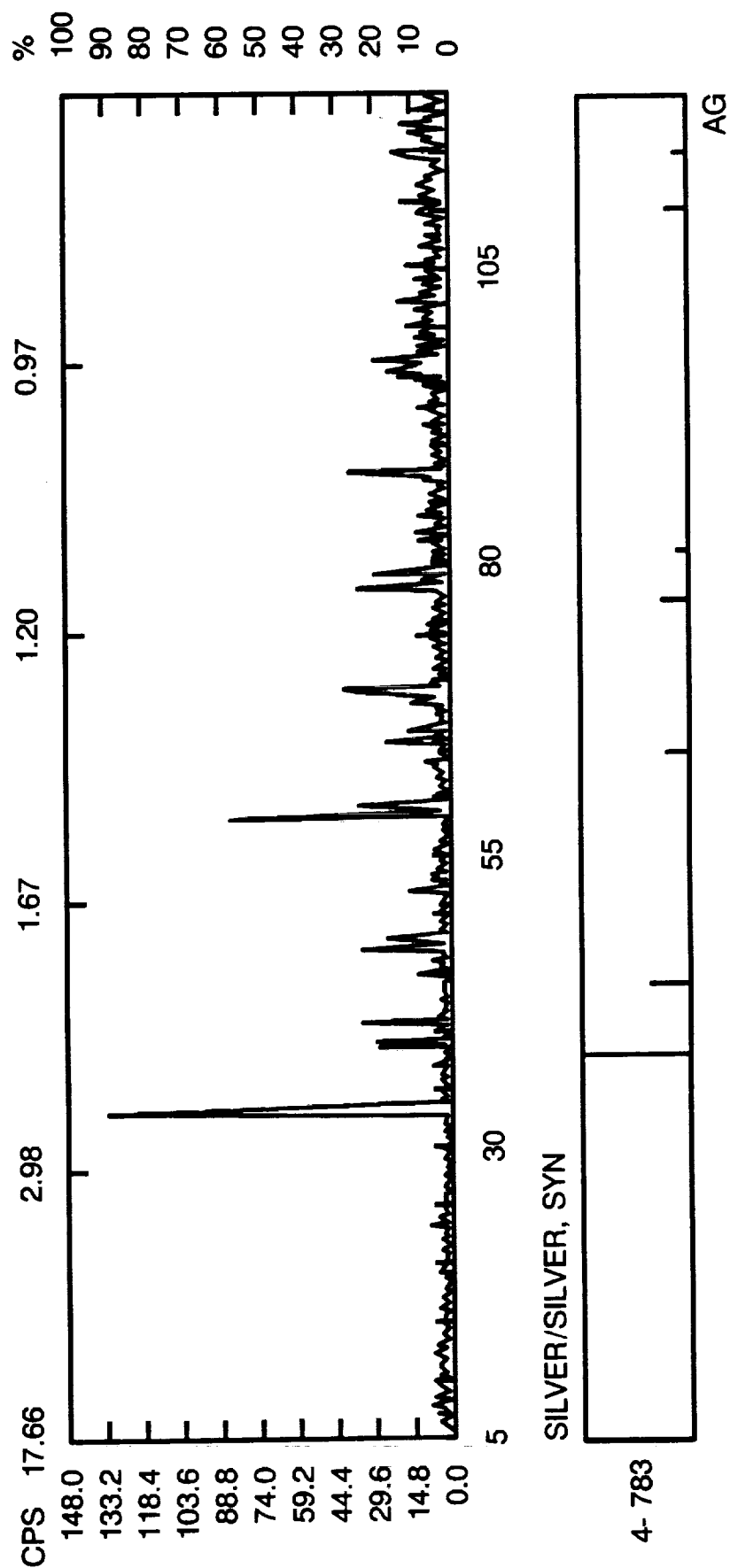


Figure 4. XRD scan of HTSC sample with 15% silver.

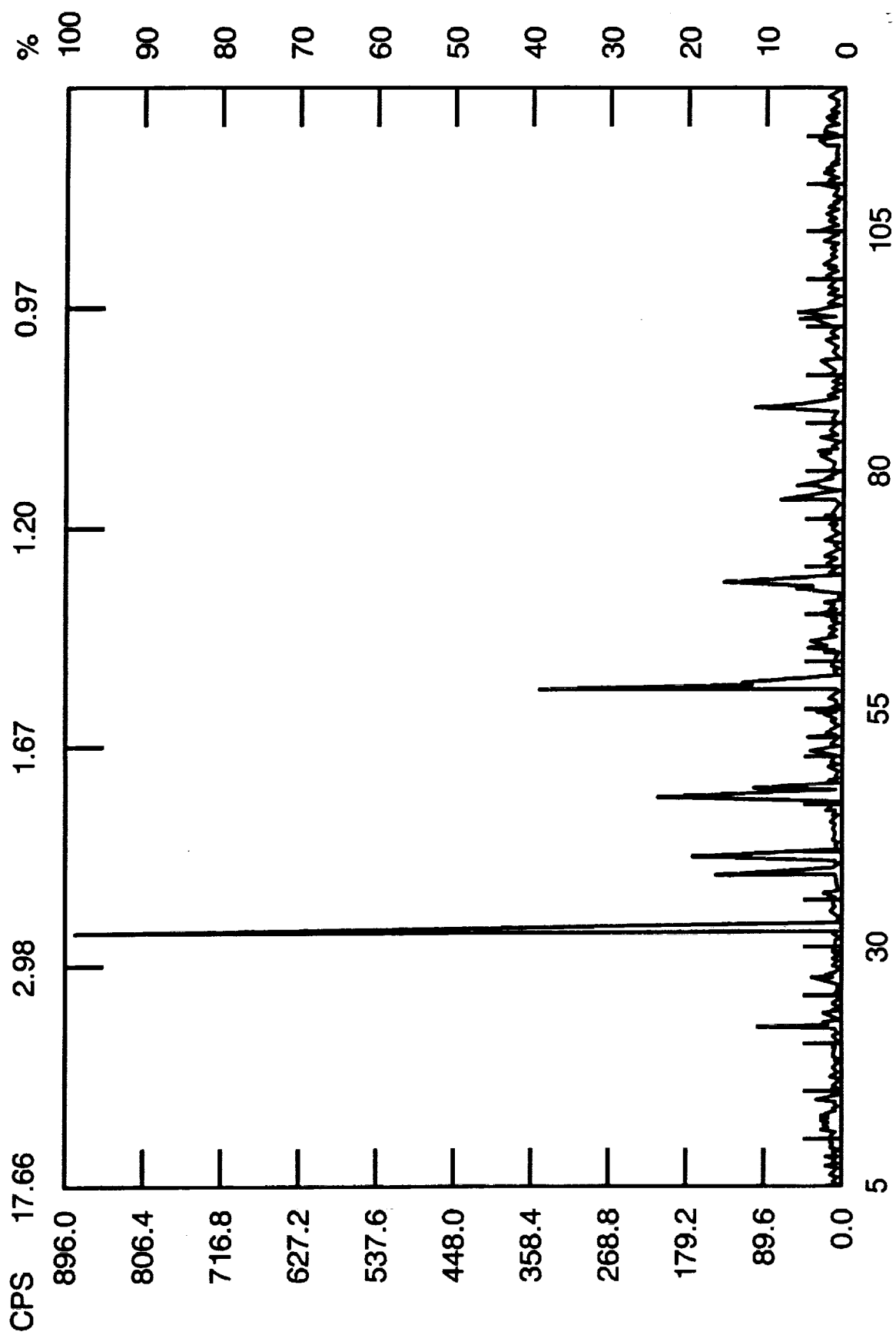


Figure 5. XRD scan of HTSC sample with trace amount of silver.

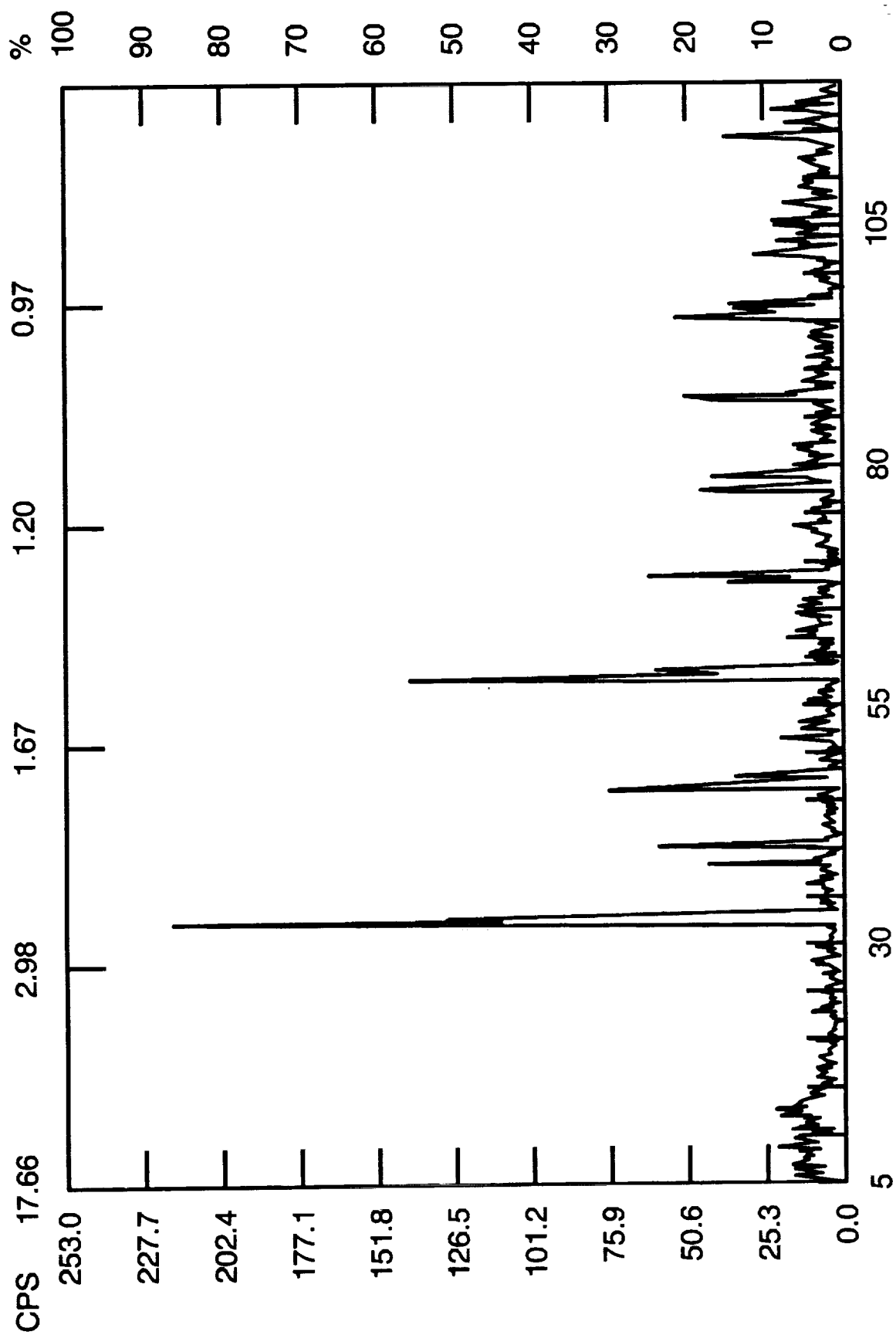


Figure 6. XRD scan of HTSC sample with Cu and Ba oxide.

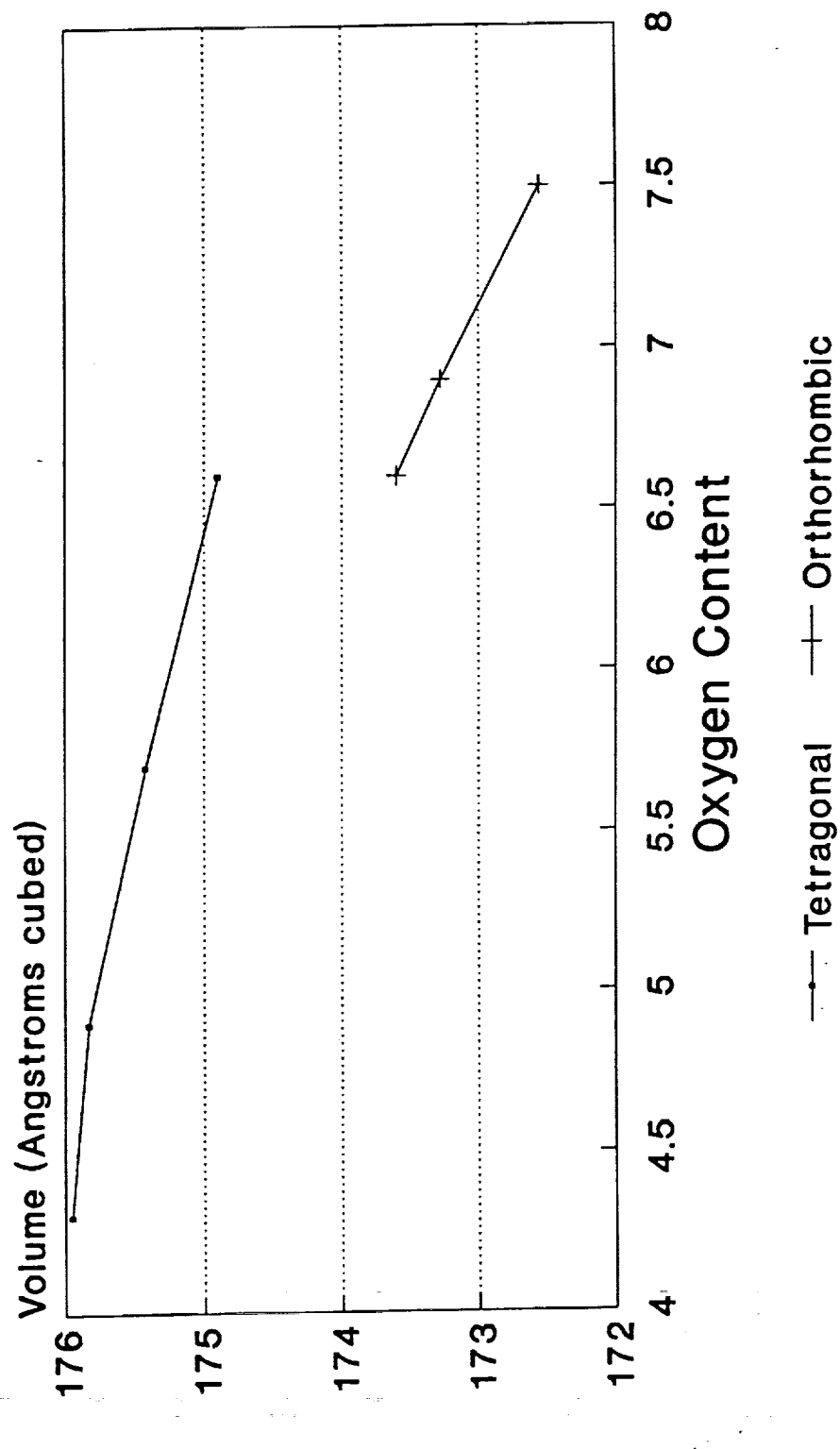


Figure 7. Unit cell volume vs. oxygen content.

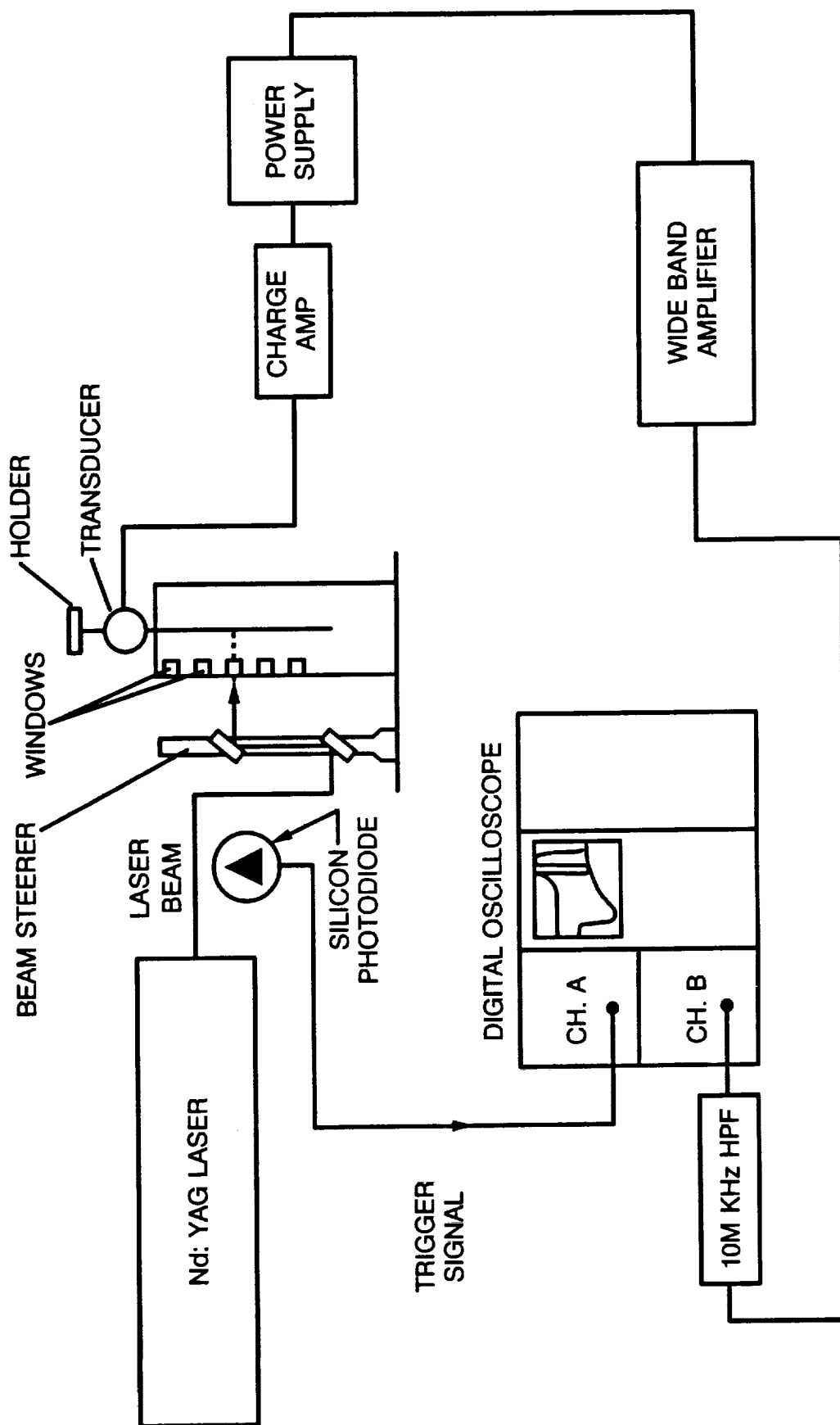


Figure 8. Sound velocity measurement system.

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